Supporting Information

Emulsion Synthesis of Size-Tunable CH₃NH₃PbBr₃ Quantum Dots: An Alternative Route toward Efficient Light-Emitting Diodes

Hailong Huang, †,‡,# Fangchao Zhao, §, # Lige Liu, † Feng Zhang, † Xian-gang Wu, † Lijie Shi, ‡ Bingsuo Zou, ‡ Qibing Pei, § * and Haizheng Zhong † *

- † Beijing Key Laboratory of Nanophotonics and Ultrafine Optoelectronic Systems, School of Materials Science & Engineering, Beijing Institute of Technology, 5 Zhongguancun South Street, Haidian District, Beijing, 100081, China
- ‡ Micro Nano Technology Center, School of Physics, Beijing Institute of Technology, 5 Zhongguancun South Street, Haidian District, Beijing, 100081, China
- § Department of Materials Sciences and Engineering, California NanoSystems Institute, Henry Samuli School of Engineering and Applied Science, University of California, Los Angeles, CA, USA

^{*}e-mail: HZ <u>hzzhong@bit.edu.cn</u>; QBP <u>qpei@seas.ucla.edu</u>

Chemicals: PbBr₂ (lead(II) bromide 99%, Aladdin), CsBr (cesium bromide 99.9%, Aladdin), methylamine (CH₃NH₂, 33 wt % in absolute ethanol, Aladdin), n-octylamine (≥99%, Aladdin), hydrobromic acid (HBr, 48 wt % in water, Aladdin), oleic acid (90%, Alfa Aesar), N,N-dimethylformamide (analytical grade, Beijing Chemical Reagent Co., Ltd., China), n-hexane (analytical grade, Beijing Chemical Reagent Co., Ltd., China), acetone (analytical grade, Beijing Chemical Reagent Co., Ltd., China), tert-butanol (analytical grade, Beijing Chemical Reagent Co., Ltd., China).

Synthesis of CH₃NH₃Br: CH₃NH₃Br was synthesized by adapting the reaction of the methylamine and hydrobromic acid. Firstly, methylamine in absolute ethanol was cooled to 0 °C with slightly excess of hydrobromic acid (the molar ratio of CH₃NH₂ and HBr was less than 1) under vigorous stirring for 2 h. Then the solution was evaporated using rotary evaporation under a pressure of 0.1 MPa at 45 °C for 30 min. The residual was washed by diethyl ether in three times and dried in a vacuum drying oven (60 °C, 5 h) for future use.

Fabrication and purification of hybrid CH₃NH₃PbBr₃ QDs: The 'aqueous phase' was made by using a mixture of CH₃NH₃Br (solution A: 0.16 mmol CH₃NH₃Br dissolved in 0.3 mL DMF) and PbBr₂ (solution B: 0.2 mmol PbBr₂ dissolved in 0.5 mL DMF). The 'oil phase' (10 mL hexane) was mixed with 0.5 mL oleic acid and n-octylamine (20 μL) to form solution C. Then the 'aqueous phase' solution A and solution B were added dropwise into solution C. Along with the mixing, emulsion was formed and the colour of solution turned from clear to milky white. After that, a

fixed amount of *tert*-butanol (1.5-8 mL) or acetone (8 mL) was used as a demulsifier to initiate a demulsion process. After that, the mixture was centrifugated at 6000 rpm for 5 min to obtain precipitates, which contain the as-prepared colloidal QDs and larger sized side-products. Then the precipitates were redissolved into 4 mL hexane to extract the colloidal QDs. After another centrifugation at 5000 rpm for 5 min, a bright yellow-green colloidal solution was obtained. The colloidal solution can be reprecipitated from the solution by adding *tert*-butanol and then dried into powder for further use. The synthesis was scaled up ten-fold to obtain 25 mg solid-state powder.

Fabrication of hybrid CsPbBr₃ QDs: The 'aqueous phase' was made by using a mixture of CsBr (solution A: 0.3 mmol CsBr dissolved in 0.3 mL deionized-H₂O) and PbBr₂ (solution B: 0.3 mmol PbBr₂ dissolved in 0.3 mL DMF). The 'oil phase' (10 mL hexane) was mixed with 2 mL oleic acid and n-octylamine (0.25 mL) to form solution C. Then the 'aqueous phase' solution B and solution A were added dropwise into solution C. Along with the mixing, emulsion was formed and the colour of solution turned from clear to slight white. After that, a fixed amount of acetone (8 mL) was used as a demulsifier to initiate a demulsion process. After that, the mixture was centrifugated at 7000 rpm for 5 min to obtain precipitates, which contain the as-prepared colloidal QDs and larger sized side-products. Then the precipitates were redissolved into 2 mL hexane to extract the colloidal QDs. After another centrifugation at 7000 rpm for 5 min, a bright yellow-green colloidal solution was obtained.

Plotting of ternary phase diagram: A 10 g mixture with of DMF and n-hexane with various mass ratios (1:9, 1:4, 3:7, 2:3, 1:1, 3:2, 7:3, 4:1, 9:1) under vigorous stirring at room temperature was tested. In order to exclude the interference of n-octylamine, 20 μL n-octylamine was added to all groups. The mixed solution was opaque due to the immiscibility of DMF and n-hexane. Then OA was added dropwise into the mixture using a 1 mL syringe. When the mixture turned from opaque into clear, we recorded the critical amount. The weight ratio of DMF, n-hexane and OA was applied to plot the ternary phase diagram.

Device fabrication and characterization: ITO-glass substrate were sequentially washed with acetone, ethanol and deionized water, followed by UV ozone treatment for 15 min. poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) solution was spin coated on the ITO film at 4000 rpm, then annealed at 150 °C for 15 min. Spin-casting method was also used for fabricating light emitters of CH₃NH₃PbBr₃ QD films. CH₃NH₃PbBr₃ QD dispersed in Tetrahydrofuran (2.5 mg/mL) was spin-coated on the PEDOT:PSS film, followed by thermal annealing at 70 °C for 15 min, then (2,2,2-(1,3,5-benzinetrily)tris(1-phenyl-1-Hbenzimidazole) (TPBi) (40 nm), CsF (1 nm) and Al (80 nm) were thermally deposited in sequence in a high-vacuum chamber with a deposition rate of 1, 0.1, and 5 Å/S, respectively (<10⁻⁶ mbar). Keithley 2400 and Keithley 2000 SourceMeter unit linked to a calibrated silicon photodiode were used to measure the current–voltage–brightness characteristics. A spectrophotometer PR-655 (Photo Research, Inc.) was used to measure the electroluminescence spectrum.

Material Characterizations: TEM images were taken using a transmission electron microscope (JEM-2100F) machine operating at an accelerated voltage of 200 kV. UV-vis absorption spectra of QDs dissolved in n-hexane was measured using UV-6100 UV-vis spectrophotometer (Shanghai Mapada Instruments Co., Ltd., China). PL spectra were taken using an F-380 fluorescence spectrometer (Tianjin Gangdong Sci. & Tech. Development Co., Ltd., China). Crystal structure of samples was examined on a Bruker/D8 FOCUS X-ray diffractometer, using a Cu Kα radiation source. The samples were scanned from 2°<20<80° at an increment of 3° /min. Atomic force microscope (AFM) was performed using Bruker Dimension 5000 Scanning Probe Microscope (SPM) in 'tapping' mode. Scanning electron microscopy (SEM) images were taken on an S-4800 microscopy (Hitachi, Ltd., Japan).

Figure S1

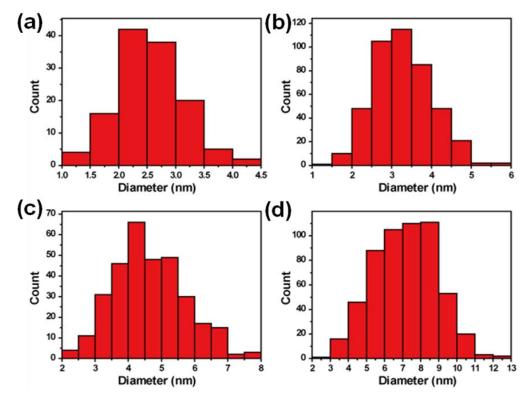


Figure S1. Size distribution of colloidal $CH_3NH_3PbBr_3$ QDs (a) 2.6 ± 0.6 nm; (b) 3.3 ± 0.7 nm; (c) 4.6 ± 1.1 nm; (d) 7.2 ± 1.7 nm.

Figure S2

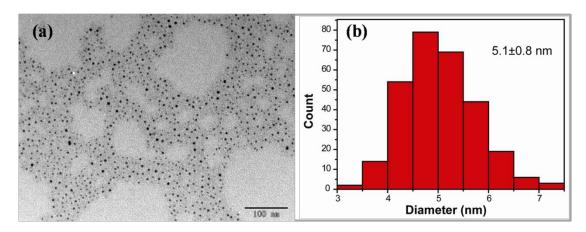


Figure S2. TEM image of 5.1 nm CH₃NH₃PbBr₃ QDs (a) and its size distribution (b).

Figure S3

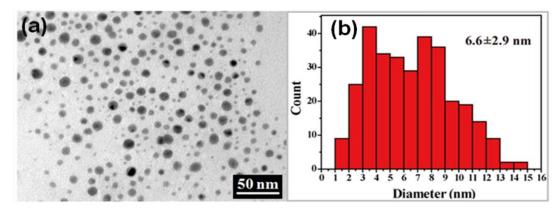


Figure S3. (a) TEM image and (b) corresponding size distribution of colloidal CH₃NH₃PbBr₃ QDs obtained by using acetone as demulsifier.

Figure S4

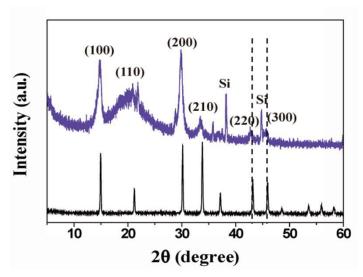


Figure S4. XRD pattern of bulk CH₃NH₃PbBr₃ (bottom) and CH₃NH₃PbBr₃ QDs (top).

Figure S5

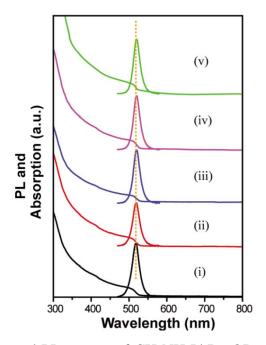


Figure S5. Absorption and PL spectra of $CH_3NH_3PbBr_3$ QDs with specified average diameter of (i) 2.6 ± 0.6 nm; (ii) 3.3 ± 0.7 nm; (iii) 4.6 ± 1.1 nm; (iv) 5.1 ± 0.8 nm; (v) 7.2 ± 1.7 nm.

Figure S6

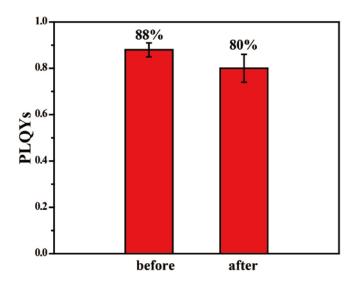


Figure S6. Absolute PLQY of CH₃NH₃PbBr₃ QDs before and after purification.

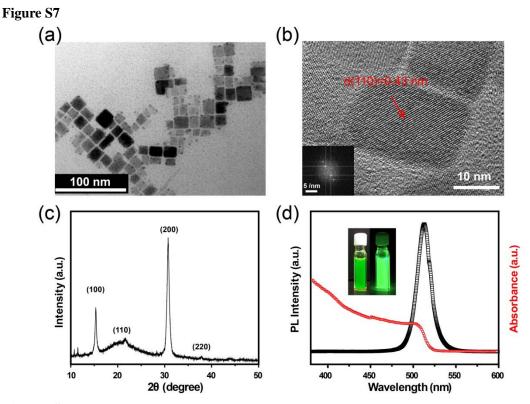


Figure S7. (a) TEM image and (b) HRTEM image of colloidal CsPbBr₃ QDs. Inset: FFT pattern transformed from the HRTEM image. (c) XRD pattern of bulk CsPbBr₃ QDs. (d) UV-Vis absorption & PL emission spectra (peak: 521 nm) of a typical CsPbBr₃ QD solution. Inset: Optical photographs of typical CsPbBr₃ colloidal solution under the emitter illuminated with ambient light (left) and UV light-lamp centered at 365 nm (right).

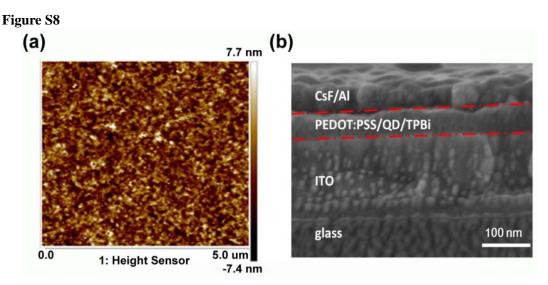


Figure S8. (a) AFM image of CH₃NH₃PbBr₃ quantum dot films. (b) the cross-sectional SEM images of a typical device.

Table S1. Comparison of the device performance between our work and the reported thin film based devices with similar device structure.

Device structure	Luminance (cd/m²)	Current efficiency (cd/A)	EQE	Peak position (nm)	Fwhm (nm)
ITO/TiO ₂ /PEDOT:PSS/MAP bBr ₃ /F8/Ca/Ag ^{ref. 1}	364	0.3	0.24%	517	≥30
ITO/PEDOT:PSS/MAPbBr ₃ / Zn _{1-x} Mg _x O/Ca/Al ^{ref. 2}	550	0.21		525	25
ITO/PEDOT:PSS/MAPbBr ₃ / TmPyPB/LiF/AL ref. 4	1500		0.1%	544	20
ITO/PEDOT:PSS/MABr ₃ -PI P/ F8/Ca/Ag ^{ref. 4}	<2000		1.2%	534	19
ITO/PEDOT:PSS/MAPbBr ₃ / PCBM/Ag ^{ref. 5}	20	0.02		515	31
ITO/PEDOT:PSS/MAPbBr ₃ - PEO composite/In-Ga ^{ref. 6}	4064	0.74	0.165%	532	23
ITO/PEDOT:PSS/PVK/CsPb Br ₃ QDs/TPBi/LiF/Al ^{ref. 7}	946	0.43	0.12%	516	23
ITO/PEDOT:PSS/MAPbBr ₃ - PVK:PBD/BCP/LiF/Al ^{ref.8}	10590		0.48%	530	20
Glass/SOCP/MAPbBr3/TPBI /LiF/Al ^{Ref.9}	>10000	42.9	8.53%	540	20
ITO/PEDOT:PSS/ MAPbBr ₃ QDs/TPBi /CsF/Al (This work)	2503	4.5	1.1%	524	24

References

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